

Determination of Arsenic in Foodstuffs contaminated by Arsenical War Gases

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Issued under the auspices of the Society of Public Analysts and Other Analytical Chemists and with the authority of the Chemical Defence Research Department (Ministry of Supply), to which Department the Society is indebted for the information and the detailed description of the recommended procedure contained in this pamphlet.

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Determination of Arsenic in Foodstuffs contaminated by Arsenical War Gases

IN the Pamphlet "Examination of Foodstuffs for War Gases" issued to members of the Society in August, 1940, it was indicated on page 5 that, where contamination by arsenical gas was suspected, the determination of arsenic should be carried out by the Gutzeit method after acid destruction of the sample and subsequent reduction of the arsenic to the tervalent condition.

Since then, several members of the Society have reported that they have experienced difficulty in determining the full amount of arsenic in samples of food contaminated with known amounts of arsenical war gases. The matter was discussed at a meeting of the Society on 2nd April, 1941, and it is hoped that the papers then read and the ensuing discussion will shortly appear in THE ANALYST.

As the matter is considered urgent, it is felt that a recommended method should be issued for the benefit of all analysts who may have to examine food contaminated by arsenical war gases. The Analytical Methods Committee of the Society have not been able to arrange for the large amount of work necessary to establish a generally applicable method, but they are authorised to circulate the following method which the Chemical Defence Research Department of the Ministry of Supply recommend as the result of their own investigation.

In issuing this method, the Committee draw particular attention to the following points, which would appear to be of special importance with food contaminated by arsenical war gas:—

1. The slow and controlled initial oxidation by a large excess of nitric acid.
2. The avoidance of any charring or local overheating.
3. The necessity for the complete removal of all nitric acid and nitrous fumes at the end of the digestion.
4. The necessity for the reduction of the arsenic to the tervalent condition before proceeding to the Gutzeit process. For this purpose the method recommends gaseous sulphur dioxide, with subsequent removal by boiling.
5. The method specifies strip matching in the Gutzeit process, but it allows also the procedure of the British Pharmacopoeia. Analysts will probably use the latter procedure,—to which they are more accustomed,—and, if so, care should be taken to check the correctness of the diameter of the disc exposed to the action of the arsine.
6. As with all Gutzeit procedures, suitably pure and sensitive zinc must be used.

Method

for the Determination of Arsenic in Foodstuffs contaminated by Arsenical War Gases.

PRINCIPLE.

The sample of contaminated foodstuff is oxidised with nitric and sulphuric acids and excess of nitric acid removed; the solution is then reduced with sulphur dioxide and the tervalent arsenic estimated by the Gutzeit method.

I. OXIDATION.

About 10 g. of the sample are introduced into a 250 ml. Kjeldahl flask, 30 ml. of conc. nitric acid (AsT.) are added and the contents of the flask are mixed by rotation. The flask is then gently warmed, with periodic rotation or mechanical shaking, until all frothing has ceased.

More nitric acid is added (about 10 ml.) followed by 5 ml. of conc. sulphuric acid (AsT.) and the heating is continued carefully, precaution being taken against local overheating and charring. If the initial digestion is too vigorous a sudden evolution of nitric oxides occurs, followed by local charring, production of sulphur dioxide and loss of arsenic. This is particularly the case with foods containing chlorides and those contaminated with lewisite. Presumably a local reduction of As^{V} to As^{III} occurs, with distillation of arsenic as trichloride from the medium. The attainment of accurate results is, therefore, dependent upon the exercise of extreme care during the initial stages of the digestion.

When practically all the organic matter has been destroyed, more vigorous heating is allowed, with addition of further quantities of conc. sulphuric acid and drop additions of nitric acid until oxidation is complete and a clear sulphuric acid solution results. The time of oxidation varies with the material, fatty substances requiring much longer periods and larger quantities of acids than others.

The contents of the Kjeldahl flask are then cooled, diluted with about 50 ml. of distilled water and, after being boiled for a few minutes, evaporated down to sulphuric acid fuming. This is to ensure the complete removal of nitric compounds which inhibit the evolution of arsine in Stage III. It is essential, therefore, that the sulphuric acid shall boil quite vigorously to sweep out all residual nitric vapours from the flask.

II. REDUCTION.

The contents of the flask, after cooling, are diluted to 25 ml. with distilled water and a steady stream of sulphur dioxide is passed into the solution for 10 minutes to reduce the arsenic to the tervalent condition.

Excess of sulphur dioxide is then removed by boiling. At this stage the solution is very prone to bump when heated and precautions must be taken to avoid loss of liquid in this way. The most satisfactory procedure is to heat on a mechanical shaker fitted with electric hot-plates.

All sulphur dioxide must be removed, otherwise hydrogen sulphide will be generated in the Gutzeit vessel and modify the resulting arsine stain.

Prolonged heating at this stage is, however, to be avoided, since the solution may become re-oxidised.

The solution is finally made up to 100 ml. with distilled water.

III. GUTZEIT DETERMINATION.

The procedure given in Appendix VIII of the British Pharmacopoeia, 1932, may be used for the determination of arsenic in the solution from Stage II, but the Sanger and Black "strip" modification described below has been found to be more satisfactory and to give more consistently reliable results.

An aliquot portion of the solution from II containing between 0.005 and 0.045 mg. of arsenic is transferred to a Gutzeit vessel (of height about 11 cm. and capacity up to the shoulder about 100 ml.). To the solution are added 3.5 ml. of conc. hydrochloric acid (AsT.) and 0.5 ml. of stannous chloride (AsT.) solution. The sulphuric acid content is then adjusted to 1 ml., allowance being made for the residual sulphuric acid from the oxidation, and the bottle is filled with water up to the 50 ml. mark.

The outlet tube of the apparatus is then prepared. A piece of specially prepared fluted lead acetate paper is placed in the bottom of the tube and glass wool soaked in lead acetate solution in the top, to ensure that no hydrogen sulphide reaches the mercuric chloride paper. The end of the outlet tube is then fitted with a narrow-bore glass tube, 10 cm. long $\times$ 0.4 cm. diameter, in which is placed a strip of mercuric chloride paper. This paper is inserted until the lower end is about 4 cm. above the bottom of the tube.

About 20 pellets (approx. $\frac{1}{4}$ inch high) of AsT. zinc are then introduced into the Gutzeit vessel and the outlet tubes immediately placed in position. The vessel is placed in a water bath maintained at about 15° C., and the gas evolution is allowed to proceed for 1 hour. The stain on the mercuric chloride paper is then fixed by dipping in molten paraffin wax (white, m.p. 60–80° C.) and compared with stains similarly prepared from standard arsenite solutions.

PREPARATION OF REAGENTS, PAPERS AND STAINS FOR THE GUTZEIT PROCEDURE.

Mercuric Chloride Papers.—Whatman filter paper (No. 1) is dipped in 1 per cent. mercuric chloride solution, drained of excess liquid and then dried, away from all hydrogen sulphide and other fumes. When dry, the outside $\frac{1}{2}$ inch is trimmed off and discarded, as this contains uneven concentrations of the mercury salt.

The paper is then cut into strips 4 mm. $\times$ 8 cm. and kept in a stoppered bottle coated with black to exclude light.

It is essential that a good quality paper be used for this purpose. Uneven thicknesses produce variable stains. A paper with a high content of reducing substances should not be used and a paper packed with kaolin or similar filler produces poor stains. The humidity of the paper is also a factor, air-dried Whatman No. 1 being the most consistent in this respect.

Stannous Chloride Solution.—80 g. of Stannous Chloride (AsT.) are dissolved in 100 ml. of water and 5 ml. of conc. hydrochloric acid are added.

Lead Acetate Paper.—Filter paper is impregnated by immersion in saturated lead acetate solution and air-dried. It is then cut into pieces 7 cm. $\times$ 5 cm. and fluted before being placed in the Gutzeit outlet tube.

Zinc (AsT.).—The zinc pellets should be of approximately $\frac{1}{4}$ inch mesh and preferably should be washed with conc. hydrochloric acid to dull the surface and kept in distilled water until required.

Standard Stains.—These are prepared by submitting solutions containing known amounts of arsenite to the above Gutzeit procedure. A range from 0.005 to 0.045 mg. of arsenic is desirable. The standard strips should be immediately waxed and mounted in order on a white card, with spaces between them to facilitate comparison with other strips. The standard stains tend to fade, particularly if exposed to light, and should for that reason be kept in the dark.

Fresh standards should be made every time a reagent is changed or a new batch of mercuric chloride papers prepared.

